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Tetrahedral Mn_{i4} cluster in silicon

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$\mathrm{Mn}_{i4}{}^{0}$ clusters were investigated by electron paramagnetic resonance in silicon specimens with initial doping concentrations between $1.5\times10^{15}\ \mathrm{P\,cm^{-3}}$ and $5\times10^{16}\ \mathrm{B\,cm^{-3}}$. In *n*-type samples and in intrinsic samples, we obtained the EPR spectrum of the well-known $\mathrm{Mn}_{i4}{}^{0}$ cluster, whereas in *p*-type material we observed an unknown EPR spectrum of cubic symmetry which we attribute to a $\mathrm{Mn}_{i4}{}^{+}$ cluster. This spectrum is highly light sensitive. Its $+/0$ level was found near midgap by photo-EPR. In highly doped *p*-type material we could prove the presence of a $\mathrm{Mn}_{i4}{}^{2+}$ center which shows no EPR spectrum, but is transformed into $\mathrm{Mn}_{i4}{}^{+}$ under illumination.

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Manganese is an important representative of the transition metals in silicon. If forms a large variety of different defects. Isolated interstitial defects like $\mathrm{Mn}_i{}^{2+}$, $\mathrm{Mn}_i{}^{+}$, $\mathrm{Mn}_i{}^{0}$, and $\mathrm{Mn}_i{}^{-}$, and also substitutional $\mathrm{Mn}_s{}^{+}$ and $\mathrm{Mn}_s{}^{2-}$ (Refs. 1 and 2), have been identified by electron paramagnetic resonance (EPR). Furthermore, complexes with acceptor doping atoms and with other impurity atoms,[3] as well as three different Mn clusters,[4–7] have been observed.

A $\mathrm{Mn}_{i4}{}^{0}$ cluster in silicon consisting of four neutral interstitial manganese atoms which form a regular tetrahedron was first reported by Ludwig, Woodbury, and Carlson.[4] This defect, as well as the other clusters, $\mathrm{Mn}_{i3}{}^{0}\mathrm{Mn}_i{}^{-}$ and $\mathrm{Mn}_{i3}{}^{+}$, were investigated later on in great detail by EPR measurements[5–7] and also by theoretical analysis.[8–10]

The energy levels of the $\mathrm{Mn}_{i4}{}^{0}$ cluster are still controversial in the literature. A level at $E_c-0.28$ eV was obtained by combined EPR and Hall-effect investigations,[11,12] whereas early Hall-effect results,[4] combined ESR and DLTS measurements,[13,14] luminescence data,[15] and photo-EPR (Refs. 5 and 16) results show a level near midgap. In the photo-EPR work, the light sensitivity of the EPR spectra seems to be different from that in other papers. These discrepancies could be due to differences in the initial doping of the silicon material. Therefore, in the present paper, we carefully reinvestigate the $\mathrm{Mn}_{i4}{}^{0}$ center in specimens with a wide range of doping concentrations.

We have investigated floating zone silicon with initial doping concentrations $1.5\times10^{16}\ \mathrm{P\,cm^{-3}}$, $7\times10^{14}\ \mathrm{P\,cm^{-3}}$, $1\times10^{14}\ \mathrm{P\,cm^{-3}}$, $2\times10^{13}\ \mathrm{P\,cm^{-3}}$, $7\times10^{14}\ \mathrm{B\,cm^{-3}}$, $6\times10^{15}\ \mathrm{B\,cm^{-3}}$, and $5\times10^{16}\ \mathrm{B\,cm^{-3}}$. Samples with dimensions of $3\times3\times10\ \mathrm{mm^3}$ were cut from [111]-oriented disks with the long axis in a [110] direction. Manganese was chemically deposited on the surface from a manganese chloride solution. The samples were annealed for 1.5–2 h at 1265 °C in a vertical furnace under a pure He atmosphere, and quenched in water with a layer of oil on top. After this treatment all specimens except those with $5\times10^{16}\ \mathrm{B\,cm^{-3}}$ were *n* type, due to the Mn doping.

The measurements were performed in dispersion, using a Bruker ER200D spectrometer in the *X* band (9.41 GHz). The magnetic field was modulated at 50 kHz. The specimens were mounted in a H_{103} optical transmission cavity, with their [110] axis perpendicular to the static magnetic field so that, by turning the crystal around this axis, the magnetic field could be swept through the entire (110) plane. The temperature was kept near 4 K with an Oxford ESR9 continuous flow cryostat. For the photoelectron-spin-resonance measurements we used a 250-W quartz-halogen tungsten lamp and a Leiss quartz-prism monochromator.

EPR results

In all originally phosphorus-doped specimens, as well as in high resistivity boron-doped specimens, we found the EPR signal of the $\mathrm{Mn}_{i4}{}^{0}$ cluster as described in previous work. Its spin Hamiltonion is

$$\mathbf{H}=g\mu_B B\mathbf{S}+1/6a[\mathbf{S}_\mathbf{x}^4+\mathbf{S}_\mathbf{y}^4+\mathbf{S}_\mathbf{z}^4-15S(S+1)(3S^2+2S-1)]+\mathbf{A}\cdot\mathbf{S}\cdot\mathbf{I},\tag{1}$$

with the total nuclear spin $I=4I_{\mathrm{Mn}}$ and $I_{\mathrm{Mn}}=\frac{5}{2}$.[4,5] The values of g and the cubic field constant a are 2.009 and $a=-4.2\times10^{-4}\ \mathrm{cm^{-1}}$, respectively.

The spectrum is composed of 12 fine-structure lines whose angular dependence in the (110) plane is given by

$$B=B_0+B_i(1-5\sin^2\theta+15/4\sin^4\theta),\tag{2}$$

where $i=1$–12, and θ is the angle between the magnetic field and the [100] direction.[17]

Due to the presence of four manganese nuclei, each of these line is split into 21 hyperfine lines with the intensity distribution[4]

$$1:4:10:20:35:56:80:104:125:140:146:140:\ldots.$$

The hyperfine structure constant is[5] $A=-13.7\times10^{-4}\ \mathrm{cm^{-1}}$.

At $\theta=29°$ and $40'$ the value of the bracket is zero, so that in this direction all fine-structure lines nearly coincide, and only the hyperfine splitting is left over. In other directions like [100] and [111], several overlapping hyperfine groups between 0.28 and 0.38 T are visible.

Immediately after quenching, we observed not only the $\mathrm{Mn}_{i4}{}^{0}$ spectrum but also the spectra of other manganese related centers, in particular that of isolated $\mathrm{Mn}_i{}^{-}$ (Ref. 12) After several weeks at room temperature the intensity of this spectrum decreased simultaneously with the formation of $\mathrm{Mn}_{i3}{}^{0}\mathrm{Mn}_{i}{}^{-}$ clusters[6] in *n*-type samples and high-resistivity *p*-type samples, while in *p*-type samples with an initial doping concentration of $7\times10^{14}\ \mathrm{B\,cm^{-3}}$ and more, the centers $\mathrm{Mn}_{i3}{}^{+}$ (Ref. 7) and $\mathrm{Mn_2B}$ (Ref. 7) and MnB pairs[18] appeared.

In order to isolate the $\mathrm{Mn}_{i4}{}^{0}$ clusters, the samples were subjected to isochronous annealing for 15 min, starting at 150 °C and increasing the temperature in steps of 25 °C. In the *n*-type and high-resistivity *p*-type samples, the signal of the $\mathrm{Mn}_{i3}{}^{0}\mathrm{Mn}_{i}{}^{-}$ cluster begins to decrease at 175 °C, and disappears at 275 °C. On the other hand, the signal of $\mathrm{Mn}_{i4}{}^{0}$ increases up to 300 °C, where it begins to decrease until at 350 °C only a weak EPR signal is left over. During this weakening of the signal, no signals from isolated Mn_{i} could be detected, indicating that at least part of the clusters begin to grow further rather than merely being dissolved.

In the highly doped *p*-type samples, first the $\mathrm{Mn_2B}$ spectrum disappears at 150 °C, and then, at 175 °C, the MnB-pairs vanish with a simultaneous increase of the $\mathrm{Mn}_{i3}{}^{2+}$ signal which begins to weaken at 250 °C and becomes undetectable above 275 °C. At the same time, a signal near 0.33 T increases, and begins to decrease only at temperatures above 300 °C.

Although this signal appears in the same field region and is similar in some respects, it is nevertheless significantly different from the $\mathrm{Mn}_{i4}{}^{0}$ signal in *n*-type material. Figure 1(a) shows this signal. The initial doping of the specimen was $6\times10^{15}\ \mathrm{B\,cm^{-3}}$, and the field was applied in the [100] direction.

We recognize essentially the same pattern of 21 hyperfine lines, which is typical of the $\mathrm{Mn}_{i4}{}^{0}$ center. This indicates that the spectrum also belongs to a cluster of four equivalent manganese atoms. With $g=2.011\pm0.003$, its g value is only slightly higher than the value of the $\mathrm{Mn}_{i4}{}^{0}$ cluster ($g=2.009$[2]), and the hyperfine constant $|A|=(13.4\pm0.2)\times10^{-4}\ \mathrm{cm^{-1}}$ also has a similar value. But here the similarity ends: The orientation dependence of the spectrum is much weaker than that of $\mathrm{Mn}_{i4}{}^{0}$. Its appearance in Fig. 1 as well as for all other directions of the magnetic field is very similar to the spectrum of $\mathrm{Mn}_{i4}{}^{0}$, which is observed for minimum fine structure splitting (i.e. under 30° to [100]). This must be due to a very small cubic field constant a, which is in fact so small that in Fig. 1(a) the fine structure manifests itself only as a small splitting of the hyperfine lines.

As a consequence, a reliable value of S cannot be extracted from the spectra, and the value of a in the Hamiltonian could only be estimated from a computer simulation with the result $a\approx0.15\times10^{-4}\ \mathrm{cm^{-1}}$. In this simulation the Zeeman term and the cubic fine-structure term of Eq. (1) are calculated by exact diagonalization, assuming $S=13/2$ (see below), whereas the hyperfine term is taken into account by second-order pertubation theory.[5] This is expected to give a good estimate of the coefficient a. The simulated spectrum is shown in Fig. 2.

Since the center exists only in *p*-type samples, and has the same thermal stability as the neutral Mn_{i4} cluster, we conclude that the spectrum is associated with a positively charged Mn_{i4} cluster. (Further proof will be given below.)

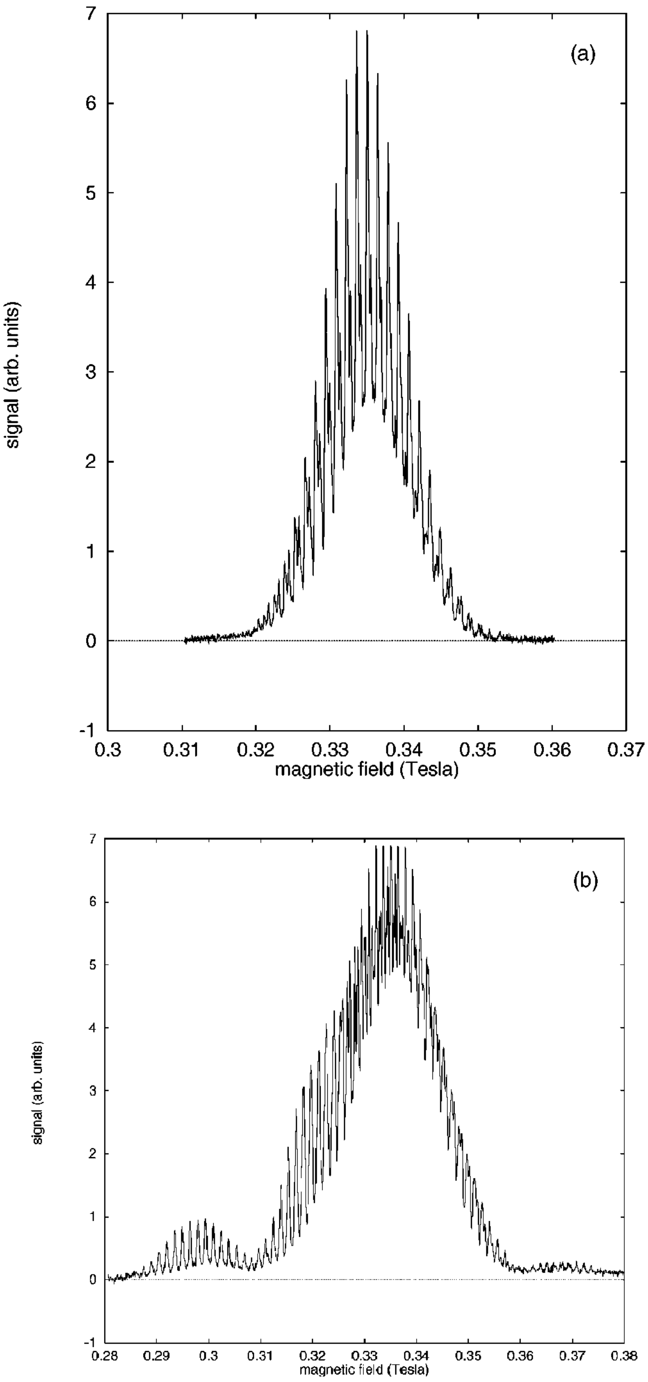

FIG. 1. EPR spectrum of a *p*-type sample after annealing at 275 °C. The magnetic field is applied in the [100] direction. (a) In the dark. (b) Under illumination.

As the d shell of a neutral manganese atom (electron configuration $3d^7$) is more than half-filled, taking away one electron increases the spin by 1/2. Consequently we assign the total spin $S=13/2$ to our spectrum.

Photo-EPR results

In contrast to the $\mathrm{Mn}_{i4}{}^{0}$ signal, which shows no obvious change under illumination, our spectrum is very sensitive to

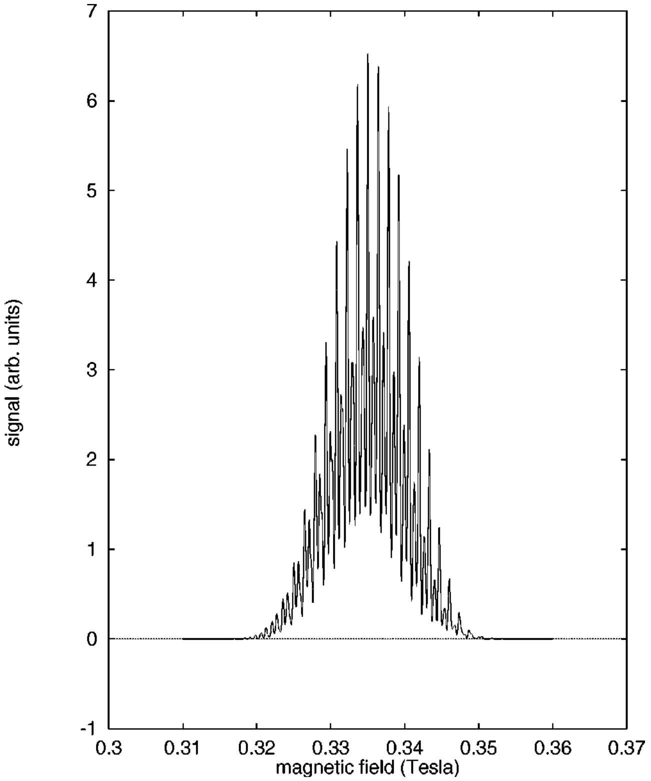

FIG. 2. Simulation of the spectrum in Fig. 1(a).

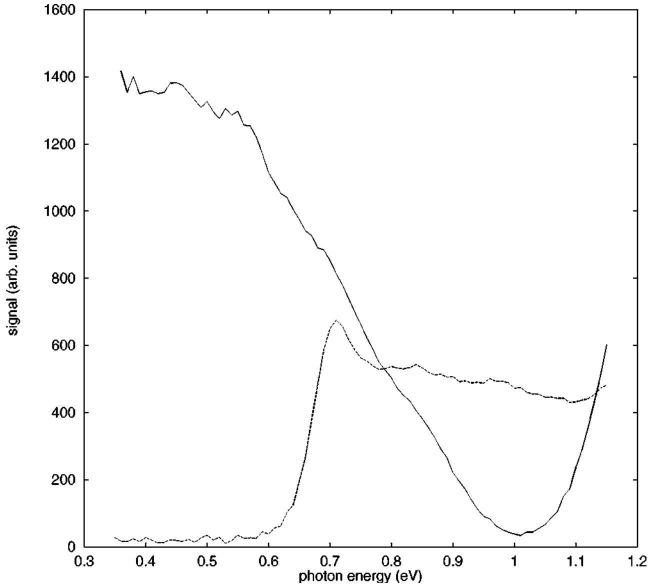

FIG. 3. Variation of the signal intensity with photon energy of the incident light for Mn$_{i4}{}^{+}$ clusters. Continuous line: original doping 7×10^{14} B cm^{-3}. Broken line: highly *p*-doped sample with 5×10^{16} B cm^{-3}.

incident light. Not only the intensity of the lines but the whole character of the spectrum changes [Fig. 1(b)]. More specifically, the characteristic wings of the Mn$_{i4}{}^{0}$ spectrum which are observed in [100] and [111] directions appear under illumination. Apparently, by capturing an electron, the center is transformed into a neutral Mn$_{i4}$ cluster. Consequently the spectrum must be due to a positively charged Mn$_{i4}{}^{+}$.

In another sample which had a boron concentration of 5×10^{16} cm^{-3}, and was the only one which remained *p* type after the Mn doping, no EPR signal could be detected after annealing at 275 °C. But, again, under illumination we obtained a mixture of the Mn$_{i4}{}^{0}$ signal and our Mn$_{i4}{}^{+}$ signal. Therefore, we conclude that a Mn$_{i4}{}^{2+}$ state exists in the gap, which shows no EPR signal but is transformed into Mn$_{i4}{}^{+}$ and Mn$_{i4}{}^{0}$ when it captures electrons.

In order to obtain information about the energy levels associated with the cluster, we have also investigated the dependence of the Mn$_{i4}{}^{+}$ signal on the photon energy in specimens with low and high boron contents. The results are represented by the two curves of Fig. 3: The signal of Mn$_{i4}{}^{+}$ from the specimen with the lower boron content begins to decrease near 0.55 eV, while the Mn$_{i4}{}^{0}$ signal (not shown here) increases in parallel. Consquently the Mn$_{i4}{}^{+}$ center must have captured an electron at this photon energy. On the other hand, the signal from the highly boron doped specimen that remains *p* type after Mn doping begins to increase near 0.61 eV, indicating that the Mn$_{i4}{}^{2+}$ which is present in this sample captures an electron.

At first sight the results are surprising: It is hardly conceivable that in both cases the electron is excited directly from the valence band to the center, because this would imply that the level of the transition $2+/+$ is above the $+/0$ level. The two results are only compatible if, in the transition at 0.55 eV, the electron is transferred indirectly via the conduction band, from where it is rapidly captured by the $+/0$ level of the cluster. (The low photosensitivity of the Mn$_{i4}{}^{0}$ spectrum indicates, in fact, that the $+/0$ level has a large capture cross section and a small absorption cross section. It could be the same level that was seen at $E_c-0.28$ eV by other authors.[11,12]) On the other hand, in a specimen with high boron content, the Fermi level is close to the valence band, all clusters are in the $2+$ state, and transitions to the conduction band are not possible for a photon energy of 0.61 eV. Therefore, we conclude that here the transition carries an electron directly from the valence band to the $+/2+$ level of Mn$_{i4}$.

Within the uncertainty of the measurements, the sum of the two transition energies is equal to the gap energy. Therefore the transition at 0.55 eV most likely carries an electron from the same $+/2+$ level to the conduction band, thereby transforming two Mn$_{i4}^{+}$ centers into one neutral cluster and one cluster with two positive charges. As an alternative, the energy of 0.55 eV could also be associated with the $2+/+$ transition of the Mn$_{i3}$ cluster[7] but, as we see no Mn$_{i3}{}^{2+}$ signal in the annealed samples, we can exclude a contribution of this cluster to the observed photo-EPR.

Of course we cannot fully exclude the possibilitiy that the electron for the transition at 0.55 eV is provided by an unidentified center which is not EPR active, but we would like to point out that, so far, our model explains all observations in a satisfactory manner without invoking other levels of unknown origin. The only level that we are not able to identify at present is the one that is responsible for the signal drop at 0.71 eV in Fig. 3. We assume that transitions, either from this level to the conduction band or from the valence band to this level, create electrons or holes, respectively, which can be captured by the ${\mathrm{Mn}_{i4}}^{+}$ centers.

In summary, we have found the EPR signal of a positively charged state of the Mn_{i4} cluster, and have obtained strong evidence for the existence of a doubly charged state, ${\mathrm{Mn}_{i4}}^{2+}$, although no EPR signal of this state could be observed. From photo-EPR measurements we could associate the transition ${\mathrm{Mn}_{i4}}^{+/2+}$ with a level near midgap. The level of ${\mathrm{Mn}_{i4}}^{0/+}$ could not be determined quantitatively from our own measurements, but its position is somewhere between the $+/2+$ level and the conduction band.

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